BADER

Chemical Properties of Di-Methyl-Arsine

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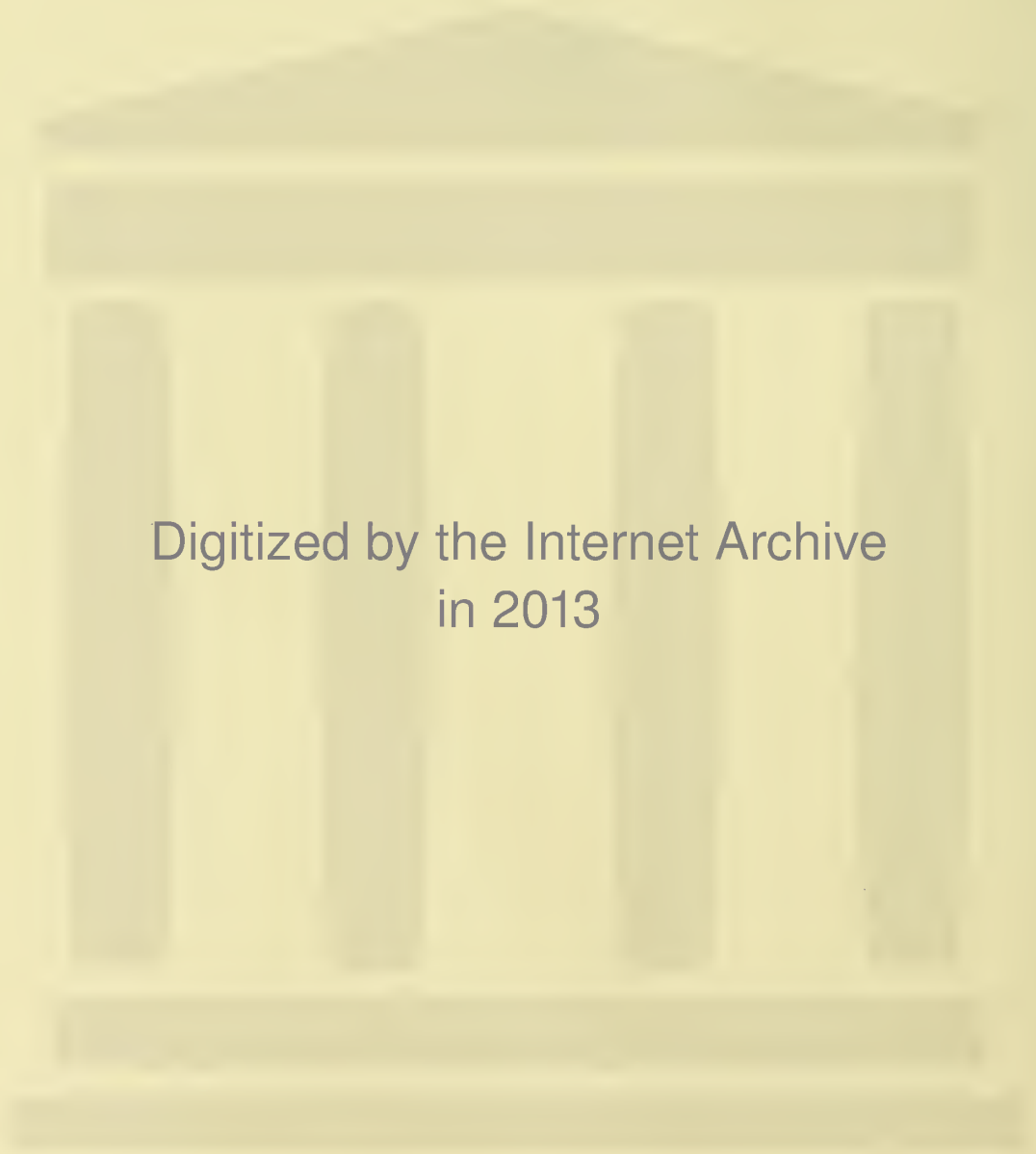

The Chemical Properties of Di-methyl-Arsine

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Will John Bader

ENTITLED The Chemical properties

of Di-methyl-arsine

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Arts

Arthur W. Palmer.

HEAD OF DEPARTMENT OF Chemistry

Introduction.

In the year 1760 the French chemist Cadet observed that a mixture of equal parts of potassium acetate and arsenious acid when distilled, yields, together with arsenious acid and acetic acid containing arsenic, a heavy brownish red liquid, which has a most frightful smell and fumes strongly in the air. This fact was confirmed by Durande, and Thenard who investigated this liquid which was termed Cadets fuming arsenical liquid. It is however to the research of Bunsen, carried on for many years that we owe an exact knowledge of the arsenical methyl compounds.

Bunsen showed that cadets liquid as well as its numerous derivatives, contains

- a radical having the formula C_2H_6As and that this substance in its chemical relations, exhibits striking analogies with a metal. He succeeded in isolating this body, and this discovery contributed largely to the development of the theory of compound radicals.

This body possesses a rightfully offensive odor and was for this reason given the name cacodyl by Berzelius. Various hypotheses have been put forward respecting the constitution of this radical. Kolbe first suggested the view that it was arsen dimethyl - $As(CH_3)_2$. This was rendered very probable by the experiments of Frankland, and this view was afterwards corroborated by Cahours, and Riche. The latter also discovered tri-methyl arsine and the tetra-methyl arsonium compounds.

But it is to Baeyer, who at a later period first prepared the arsen mono methyl compounds that we are indebted for the full explanation of the relations which these various bodies bear to one another.

The arsenic compounds of methyl and of the other alcoholic radicals played an important part in the development of theoretical views not only because they furnished us with the first example of an isolable organic radical but also because they served as a means of more exactly illustrating the meaning of the term chemical valency.

Arsenic is quite metallic in its character. its alkyl compounds constitute the transition from the nitrogen and phosphorus bases to the so called metallo-organic derivatives,

that is the compounds of the alkyls with the metals.
Because of this relation between the alkyl compounds of arsenic, nitrogen and phosphorus the properties of the two latter classes of compounds may at this stage be studied

The Amines

Alkylamines are those bodies which result from the introduction of one, two & three univalent alkyls into ammonia, for the same number of hydrogen atoms.
Accordingly as one, two & three atoms of the ammonia are replaced, primary, secondary and tertiary amines are formed.
These are also sometimes called amide imide, and nitrile bases.
Derivatives also exist which correspond to the ammonium salts, and hypothetical ammonium

hydroxide (NH_4OH). These are called quaternary alkyl ammonium compounds.

The existance of alkylamine bases was very definately predicted by Liebig in 1842; and in 1849 Wurtz discovered a method for the preparation of primary amines. Shortly after, in 1851, A. W. Hofmann by the action of cyanogens on ammonia discovered a reaction which made possible the preparation of primary secondary and tertiary amines and the alkyl ammonium bases. Since that time numerous other methods of preparation have been found.

General Properties of the amines

These bodies resemble in all essential particulars like ammonia. The lower members are gases, with an odor similar to that of ammonia, are very readily

soluble in water, and give thick fumes with hydrochloric acid.

All amines when in the state of vapor, burn in air with a continuous flame, while ammonia can only be got to burn continuously in oxygen.

The higher members are liquids readily soluble in water and only the highest are sparingly soluble. Many amines possess the power of forming hydrates with water, accompanied by very considerable rise in temperature. They can be dried over potash.

As regards their basic powers, they exceed ammonia and their positive energy increases with the number of atoms of hydrogen replaced by alcohol radicals. Ammonia is therefore expelled from its compounds by the amines. Like ammonia, they unite directly with acids to form salts, which differ from

ammonical salts by their solubility in alcohol. They combine with some metallic chlorides and form compounds perfectly analogous to the ammonium double salts.

The reactivity of the primary and secondary amines as compared with the tertiary amines is dependent upon the ease with which the ammonia hydrogen atoms not substituted by alcohol radicals are replaced; therefore the primary and secondary amines in many reactions behave like ammonia.

Primary and secondary amines like ammonia are transposed by acid esters, with the formation of mono- and di alkylized acid amides: are converted by organic acid chlorides, as acetyl chloride, into mono and di alkyl acid amides; they combine with many inorganic and organic acids

anhydrides - as sulphur trioxide, acetic anhydride - to form amic acids, and are then transposed into acid amides.

Chlorine, bromine and iodine react with primary and secondary amines, either alone, or in the presence of caustic alkali, yielding alkylamine halides.

The primary alkylamine monohalides are more unstable than the dihalides, and the secondary halogen amines. Diethylamine iodide $(C_2H_5)_2NH_2I$ and dimethylamine iodide $(CH_3)_2NH_2I$, are examples of the compounds formed in this manner.

The Alkylic Phosphines

Phosphine has slight basic properties. The phosphines obtained by the replacement of the hydrogen of PH_3 by alkyls, have more of the basic character of ammonia, and approach the amines in this respect.

The basic character increases with the number of alkyl groups. They show the property of uniting with acids only in a very diminished degree, the power of uniting with acids increasing with increased replacement of hydrogen by alcohol radicals. They oxidize very energetically on exposure to the air, usually with spontaneous ignition.

The salts of the primary phosphines are decomposed by water, while caustic potash is required for the decomposition of the salts of the secondary and tertiary phosphines.

They combine readily with sulphur, and with the halogens. They are colorless, strongly refracting extremely powerful-smelling volatile liquids. They are scarcely soluble in water, but dissolve readily in alcohol and ether, oxidize very readily and show neutral reaction.

While the main products of the reaction of ammonia on

alkylic iodides are primary amines. by passing phosphine into heated alkylic iodides, no primary or secondary phosphines are formed, but only tertiary and quaternary phosphonium iodides.

In order to obtain the primary and secondary phosphines, phosphonium iodide and alkylic iodides must be heated with zincic oxide.

Arsenic Alkyl Compounds

The compounds of arsenic with the alcohol radicals show some similarities to the nitrogen compounds. The quaternary arsonic salts derived from the strongly basic tetraalkyl arsonic hydrates agree completely in chemical character with the corresponding ammonic compounds.

The similarity to the amines and phosphines is observed

in the tertiary arsines as $(CH_3)_3$, but these do not possess basic properties, nor do they unite with acids. They show in a marked degree, the property of the tertiary phosphines in their uniting with oxygen, sulphur, and the halogens, to form compounds of the type as $(CH_3)_3X_2$.

The compounds in which arsenic is triad are mostly volatile without decomposition; those in which it is pentad decompose at more or less high temperatures, losing one alcohol radical, and one halogen atom, in the case of halogen compounds. This decomposition occurs especially readily with the halogen compounds, and the temperature of decomposition is the lower, the fewer alcohol radicals, and the more halogen atoms the molecule contains.

All alkyl arsenic compounds are in the highest degree poisonous.

Arsenic alkyl compounds may be made by the distillation of potassium acetate and arsenious acid

$$+ CH_3CO_2K + As_2O_3 = [(CH_3)_2\ As]_2O + 2CO_3K_2 + 2CO_2,$$

by action of zinc alkyls upon arsenic trichloride; by the action of the alkyl iodides upon sodium arsenide; and by the transposition of tri-sodium arsenite by alkyl iodides.

Di-methyl arsine was first prepared by A. W. Palmer. The method was to reduce cacodyl chloride. Granulated zinc slightly platinized was covered with pure alcohol, and enough hydrochloric acid added to cause a rapid evolution of hydrogen. Then a mixture of cacodyl chloride, hydrochloric acid and alcohol was added in small portions. After washing and drying the resulting gas, it was condensed in a suitable vessel, by immersing the latter in a mixture of ice and

salt. Di-methyl arsine is a colorless liquid with a boiling point of 36-37°. It has the characteristic cacodyl odor, and ignites when brought in contact with the air.

The formation takes place in the following manner

$$(CH_3)_2As_2Cl + H_2 = (CH_3)_2As_2H + HCl.$$

Mono-methyl arsine is prepared by reducing sodium methyl arsenic acid by means of amalgamated zinc and hydrochloric acid. The gas given off is passed through washing and drying tubes, and is condensed in a condensation flask, which has been surrounded with solid carbon dioxide. The condensed liquid is collected from time to time in small bulbs.

Mono-methyl arsine is a colorless liquid which boils at +2° at 755 mm. pressure. It possesses the characteristic cacodyl odor, but does not take fire of itself.

when brought in contact with air, as the di-methyl compound does, but it may be ignited, and then burns with the formation of thick white clouds. On contact with oxygen it oxidizes to methyl arsenic acid - $CH_3AsO(OH)_2$, and is oxidized by nitric acid to arsenious acid.

Experimental.

Object.

The alkyl arsenic compounds have been considered as having acid properties, or as being neutral. The object of this thesis is to attempt to prove that they have basic properties, and that they react with acids to form salts, in the same manner as the amines and phosphines.

Reaction with hydriodic acid

Hydriodic acid was prepared in the following manner.
Washed hydrogen sulphide was passed into water in which a little finely powdered iodine was suspended; more iodine was added little by little, and the passage of the gas continued until the brown color of the solution disappeared.
The sulphur was filtered out, and the liquid distilled; the portion of the distillate which came over at 126°-128° was made use of in the preparation of the gaseous acid
Two parts of powdered iodine were dissolved in one part of the aqueous solution of hydriodic acid, and the solution was dropped from a separating funnel on to amorphous phosphorus, (contained in a flask), moistened with the hydriodic acid. The acid produced was passed into a large U shaped tube containing

glass beads and moistened amorphous phosphorus. (to convert any iodine vapor into PH_3) and through another tube containing fused calcium chloride. The flask containing the phosphonium was only very gently warmed.

A small bulb of dimethyl arsine was placed in a cylinder, through which the gas passed. By means of a thin glass rod, which slipped through the stopper of this cylinder, the bulb could be broken at the proper moment. The hydriodic acid gas in entering the cylinder, passed through a phosphoric anhydride drying tube and on the other side of the cylinder, passed through another phosphoric anhydride, and calcium chloride tube. These drying tubes excluded all traces of moisture from the cylinder.

The gas was then passed into two Woulfe bottles, containing water, and so arranged that the air could not be drawn back into the apparatus,

By means of a rude delivery tube the gas could be led into a eudiometer, and the volume of the gas measured.

The air in the apparatus was completely expelled and replaced by hydriodic acid gas, and the bulb of di-methyl arsine broken by means of the glass rod. Immediately a reaction took place, and a white crystalline substance was formed and deposited on the sides of the cylinder. After standing a few moments, the substance began to decompose, as was shown by a gradual change from the crystalline solid compound, to a liquid, from which bubbles of gas were given off. The gas thus formed was collected in the eudiometer. The liquid in the cylinder ceased to give off a gas after a time. The evolution of the gas, or the decomposition of the substance was much hastened by placing the cylinder in a beaker of water at 50°.

Wt. of substance taken .2704 g.
$t°$ 21°
H. of barometer 745.6
Aq. tension for 21° 18.5 m.m.
Vol. of gas given off 62.2 c.c.

$$V = \frac{62.2(722.6 - 18.5)}{760(1 + .00367 \cdot 21)} = 53.50 = \text{corrected volume.}$$

1 c.c. H = .00896 g. × 53.5 ÷ .2704
= 1.99 % H.

% found = 1.99.
Theoretical amount = 1.88.

The gas was then examined, and found to be hydrogen; since it burned off completely, with a colorless flame. Small traces of di-methyl arsine were present, which were removed by means of alcohol.

Action of Hydrobromic Acid.

Hydrobromic acid gas was prepared by dropping ten parts by weight of bromine, contained

in a separatory funnel, into a mixture of one part of amorphous phosphorus and two parts of water, in a flask.

The gas was passed into a U tube containing amorphous phosphorus moistened with hydrobromic acid, to free it from bromine vapors. The rest of the apparatus was precisely of the same form as that used in the hydriodic acid reaction.

When the bulb was broken a slight white cloud was visible, but this soon disappeared, and a liquid formed on the bottom of the cylinder. This liquid decomposed, with an evolution of gas, which was collected and measured in a eudiometer tube.

The experiment was repeated, the cylinder being immersed this time in a beaker filled with a freezing mixture of ice and salt.

When the bulb was broken, a white crystalline substance

deposited itself over the walls of the cylinder, and then decomposed with evolution of gas, after having formed a liquid. The decomposition was hastened by warming.

When the gas was collected a yellow deposit was formed on the walls of the eudiometer, which seemed to show the presence of di methyl arsine, in the gas.

The gas was then transferred, by means of a pneumatic trough, to a gas burette, and then tested for di-methyl arsine by passing into a Hempel pipette, which was charged with a ten per cent solution of ammonio-nitrate silver nitrate. Treatment with this removed the dimethyl arsine and the diminution in the volume of the gas, represented the volume of di-methyl arsine present.

Volume of gas = 40.6 c.c.

After treatment with $\frac{1}{3}$ solution, the volume was 30.00 c.c. which showed

that the gas contained 13.8 o/o of unchanged di-methyl arsine.

After the di-methyl arsine had been removed from the gas, a measured quantity of the gas was transferred to an explosion pipette, and mixed with five times its volume of air. The mixture was exploded by means of an electric spark, and the diminution in volume noted, by passing the resulting gas back into the measuring tube

Found. 5.2 c.c. of H and 8.1 c.c. of air.
Total volume = 95.6 c.c.

After explosion, volume of gas was 75.00 c.c.
Contraction = 20.6 c.c.

7.6 c.c. of Oxygen united with the hydrogen. Therefore the real contraction is 13.0 c.c., which represents the volume of hydrogen present in the gas.

The gas from this determination was passed through a pipette containing a 10 o/o potassium hydroxide solution, in order to absorb any carbon-dioxide which might

have been present, but no perceptible diminution in the volume of the gas took place.

These tests showed that the gas, after the removal of the methyl arsine, consisted of pure hydrogen.

The reaction with hydrobromic acid was repeated three times. The object of trying this reaction, was to see if the hydrobromic acid reacted in the same way that the hydriodic acid did.

Results.

	Trial 1	Trial 2	Trial 3.
Wt. taken	.2357	.5181	.1561
Vol. of gas.	20.1	77.2	9.7
Ht. of Bar.	755.5	743.4	743.1
T.	22.5°	25°	23°
Ht. of H_2O col.	23.5 in.	9 in	26.5 in.
Aq. ten.	20.3	23.55	20.85
S_1 gas.	.642	1.10	.43

Conclusion

The reaction between di-methyl arsine and hydriodic acid takes place quantitatively according to the following equation

$(CH_3)_2AsH + HI = (CH_3)_2HAsI = (CH_3)_2AsI + H_2$.

The reaction between the di-methyl arsine and hydro-iodic acid does not take place at the ordinary temperature, but it does take place at a lower temperature. At the temperature at which the experiment was carried on, the equation did not take place quantitatively, but from the appearance of the resulting compound, and the manner of its decomposition, it is evident that the reaction would proceed, under the proper conditions, in the same manner as the reaction with hydriodic acid.

The work seems to show that di-methyl arsine has basic properties, since it reacts with acids to form salts, although these salts are very unstable.